

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE THE APPLICATION OF: WASHIO, ET AL.

APPLICATION NO.: 10/578,398

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GROUP ART UNIT: 1795

EXAMINER: WALKE, AMANDA C

TITLE: THICK FILM PHOTORESIST COMPOSITION AND METHOD OF
FORMING RESIST PATTERN

DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
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Sir:

I, Yasushi WASHIO, do hereby declare that:

I have been an employee of Tokyo Ohka Kogyo Co., Ltd., Japan, the assignee of the above-identified United States patent application, since April 1, 1996, being engaged in research and development work relating to resist compositions and other related products of the company;

I am one of the applicants of the above-identified application and I am well familiar with the present case;

I carried out experiments to demonstrate the criticality of (a) from 61 to 90% by weight of a structural unit derived from dicyclopentanyl (meth)acrylate ester as recited in claim 13 of the present application for improving the alkali developability for a negative thick film photoresist composition; and

I have a good knowledge of the English language and have read and understood the application papers and the prosecution history of this and the antecedent applications as well as the Examiner's references cited therein.

PURPOSE, METHOD AND RESULTS

(1) Purpose of the Experiments:

The purpose of the Experiments described in this declaration is to show the criticality of (a) from 61 to 90% by weight of a structural unit derived from dicyclopentanyl (meth)acrylate ester as recited in claim 13 of the present application for improving the alkali developability for a negative thick film photoresist composition.

(2) Method and Results of Experiments:

Method:

(i) Production of resist compositions

100 parts by weight of each of a series of resin components produced by radical polymerization of the monomers shown below in Table A was mixed with a series of other components in accordance with the compositions described below, thus yielding a series of resist compositions.

Of the resist compositions described below, sample A represents an example of a resist composition within the scope of the present invention. Samples I, J and K are comparative examples which are outside the scope of the present invention.

Resist composition photopolymerization initiator [component (C)]:

8 parts of 2,2-dimethoxy-1,2-diphenylethan-1-one (product name: IRGACURE 651, manufactured by Ciba Geigy Corporation)

4 parts of the dimer of 2-(o-chlorophenyl)-4,5-diphenylimidazole

Polymerizable compound with an ethylenic unsaturated double bond [component (B)]:

30 parts of EO (ethylene oxide) modified trimethylolpropane triacrylate (product name: ARONIX M-350, manufactured by Toagosei Co., Ltd.)

10 parts of polyethylene glycol diacrylate (product name: NK ester A-200, manufactured by Shin-Nakamura Chemical Co., Ltd.)

10 parts of N-vinylpyrrolidone (product name: ARONIX M-150, manufactured by Toagosei Co., Ltd.)

Other additives:

0.1 parts of the polymerization initiator methylhydroquinone

Organic solvent [component (D)]:

50 parts of PGMEA

50 parts of MIBK

Table A

Monomer compositions for the component (A)

Component monomers (parts by weight)	Sample A	Sample I	Sample J	Sample K
dicyclopentanyl methacrylate	73	58	95	-
cyclohexyl methacrylate	-	-	-	73
methacrylic acid	12	12	2	12
2-hydroxyethyl methacrylate	7	14	1	7
n-butyl acrylate	4	8	1	4
2-methoxyethyl acrylate (n=1)	4	8	1	4
weight average molecular weight of resin component	20,000	20,000	20,000	20,000

(ii) Formation of resist layer, exposure, developing, and plating formation

The formation of the resist layer (application and prebaking), exposure, developing (formation of the resist pattern), formation of the plating, and stripping of the residual resist pattern were conducted under the conditions described below.

Substrate: 5 inch copper substrate

Resist layer thickness: 65 μm

Prebake conditions: 10 minutes at 110°C

Exposure conditions: CANON PLA501F HARDCONTACT exposure apparatus (product name, manufactured by Canon Corporation), exposure dose 1000 mJ/cm²

Developing conditions: 5 minutes immersion in 0.8% aqueous TMAH solution

Plating conditions: copper plating solution, product name CU200 (manufactured by EEJA Ltd.), 90 minutes immersion at 23°C, plating thickness 40 μm

Resist pattern stripping: stripping solution STRIP-710 (product name, manufactured by Tokyo Ohka Kogyo Co., Ltd.), 80°C, 20 minutes immersion

(iii) Evaluations

The adhesion of the resist pattern following developing, the resolution of the resist pattern, the degree of developing residue left following developing, the plating characteristics (wetting characteristics), and the removability of the resist pattern were evaluated using the criteria shown below. The results are shown in Table B.

The adhesion was evaluated using a dot pattern that was formed with varying dot sizes (ranging from 20 to 80 μm at intervals of 10 μm).

The resolution was evaluated using a hole pattern that was formed with varying hole sizes (ranging from 20 to 80 μm at intervals of 10 μm).

- Adhesion

O: The adhesion of dot patterns of no more than 30 μm is favorable.

Δ : The criterion for the evaluation O is not satisfied, but the adhesion of dot patterns of no more than 60 μm is favorable.

x: No dot patterns remain following developing.

- Resolution

O: No residues remain within hole patterns of no more than 30 μm .

Δ : The criterion for the evaluation O is not satisfied, but no residues remain within hole patterns of no more than 60 μm .

x: The inside of holes remain unresolved at all pattern sizes.

- Developing residues

O: No resist residues remain on the substrate.

Δ : Minimal resist residues remain on the substrate.

x: Considerable resist residues remain on the substrate.

Plating characteristics

O: Straight copper plating is possible.

Δ : The speed of copper plating is a little slow.

x: The speed of copper plating is slow.

Removability

O: Stripping is possible in 20 minutes at 80°C.

Δ: Stripping residues remain following stripping for 20 minutes at 80°C.

×: Stripping impossible.

Table B

Evaluation factor	Sample A	Sample I	Sample J	Sample K
Adhesion	O	Δ	O	Δ
Resolution	O	×	×	Δ
Developing residues	O	Δ	×	O
Plating characteristics (wetting)	O	Δ	Δ	O
Removability	O	O	Δ	O

Results:

As seen from the results, sample A which was within the scope of the present invention exhibited excellent properties with respect to adhesion, resolution, developing residues, plating characteristics and removability.

On the other hand, with respect to sample I in which the amount of dicyclopentanyl methacrylate used was just below the lower limit of the specific range of 61 to 90% by weight recited in claim 13 of the present application, it was found that adhesion, resolution, developing residues and plating characteristics were inferior to those of sample A. In particular, sample I exhibited poor resolution.

With respect to sample J in which the amount of dicyclopentanyl methacrylate used was just above the upper limit of the specific range of 61 to 90% by weight recited in claim 13 of the present application, it was found that resolution, developing residues, plating characteristics and removability were inferior to those of sample A. In particular, sample J exhibited poor properties with respect to resolution and developing residues.

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With respect to sample K in which the same monomers as those used for sample A were used in the same amounts, except that cyclohexyl methacrylate was used instead of dicyclopentanyl (meth)acrylate, adhesion and resolution were inferior to those of sample A.

(3) Conclusion

From the results of the experiment, it can be fairly concluded that the use of (a) from 61 to 90% by weight of a structural unit derived from dicyclopentanyl (meth)acrylate ester as recited in claim 13 of the present application is critical for improving the alkali developability for a negative thick film photoresist composition.

I further declare that all statements made herein to our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Yasushi WASHIO

Signature (Yasushi WASHIO)

February 9, 2009

Date